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(54) Process for preparing stable high basicity aqueous solutions of basic aluminium chlorosulphate or basic aluminium chloride

(57) Process for preparing stable aqueous solutions of basic aluminium chlorosulphate or basic aluminium chloride having a high basicity of 50-65% and high Al_2O_3 title up to 19% by weight, which comprises treating with subdivided metallic aluminium, aqueous solutions having a low basicity of 33-42%, of basic aluminium chlorosulphate or basic aluminium chloride, previously diluted with water and optionally acidified with H_2SO_4, at temperatures of 80°-105°C. The obtained solutions are suitable as coagulants in waters treatment.

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Description

The present invention relates to a process for preparing stable aqueous solutions of basic aluminium chlorosulphate or basic aluminium chloride having a Cl/Al molar ratio from 0.90 to 1.22, a SO_4/Al molar ratio from 0.02 to 0.15 in the case of basic aluminium chlorosulphate, a 50-65% basicity according to the formula

$$\frac{\%\text{ by weight } Al_2O_3/17-(\%\text{ by weight Cl}/35.5 + \%\text{ by weight } SO_4/48)}{\%\text{ by weight } Al_2O_3/17} \times 100,$$

an Al_2O_3 title up to 19% by weight and a content of calcium lower than 0.05% by weight.

Said solutions, even though with an Al_2O_3 title around 10% by weight, are known, as well as their utility in waters treatment. They are generally prepared by a process which comprises:

a) the deep etching of $Al(OH)_3$ with HCl and H_2SO_4 aqueous solutions, at the boiling point (about 113°C);
b) the subsequent treatment of the solution obtained with $CaCO_3$ to lower the level of the SO_4 ions, with $CaSO_4$ precipitation;
c) separation of $CaSO_4$ from the solution by filtration and/or centrifugation.

Such process results critical and expensive since the formation of remarkable amounts of $CaSO_4$ requires additional and expensive filtration and/or centrifugation operations and the need to dispose of the so separated $CaSO_4$.

It has now been found a process for obtaining stable aqueous solutions of basic aluminium chlorosulphate having high basicity which does not require expensive filtration and/or centrifugation operations since by-products, which must be successively separated, do not form.

The process according to the present invention comprises treating with subdivided metallic aluminium, low basicity aqueous solutions of basic aluminum chlorosulphate or basic aluminium chloride, previously diluted with water and optionally acidified with H_2SO_4, at temperatures of 80°-105°C and at atmospheric pressure with obtainment of stable high basicity solutions of basic alluminium chlorosulphate or basic aluminium chloride suitable for waters treatment.

Such process in one single phase results therefore simple and cheap both for plant and operating costs, moreover it allows to obtain stable, more concentrated solutions of basic aluminium chlorosulphate, i.e. having an Al_2O_3 title higher than that of the known stable solutions, with considerable savings in transport costs of said solutions to the user.

Object of the present invention is therefore a process for preparing stable aqueous solutions of basic aluminium chlorosulphate or basic aluminium chloride having a Cl/Al molar ratio from 0.90 to 1.22, preferably of 1.07, a SO_4/Al molar ratio from 0.02 to 0.15 and preferably of 0.13 in the case of basic aluminium chlorosulphate, a 50-65% basicity, preferably of 56% calculated according to the formula

$$\frac{\%\text{ by weight } Al_2O_3/17-(\%\text{ by weight Cl}/35.5 + \%\text{ by weight } SO_4/48)}{\%\text{ by weight } Al_2O_3/17} \times 100,$$

a Al_2O_3 title up to 19% by weight and a content of calcium lower than 0.05% by weight, comprising:

A) dilution with water of aqueous solutions of basic aluminum chlorosulphate or basic aluminum chloride having a Cl/Al molar ratio comprised between 1.6 and 2.0, a SO_4/Al molar ratio from 0.0 to 0.05, a basicity from 33 to 42% and an Al_2O_3 title of about 17% by weight, until diluted solutions having an Al_2O_3 title from 11.8 to 13% by weight are obtained;
B) acidification of the solution obtained in (A) with H_2SO_4 in amounts from 0 to 0.41 moles per mole of Al_2O_3 of the solution;
C) heating the solution at a temperature from 80° to 105°C, preferably from 80° to 95°C, subsequent slow addition of from 0.9 to 1.98 gramatoms of subdivided metallic aluminium per mole of Al_2O_3 of the solution, by maintaining the temperature at values not higher than 105°C, preferably from 80° to 95°C, until complete dissolution of the metallic aluminium;
D) optional dilution with water of the solution obtained in (C) until an Al_2O_3 title of about 10% by weight.

The acidification step (B) with H_2SO_4 can be optionally carried out at the end of the dissolution of the metallic aluminium after step (C).

The aqueous solutions of basic aluminium chlorosulphate or basic aluminium chloride having a basicity from 33 to 43%, used as starting substances in step (A), are known and commercially available, such as for instance ALPOCLAR$^{(R)}$ 200 manufactured by Ausimont S.p.A.

The subdivided metallic aluminium introduced in step (C) can be in the form of chips, granules or powders.

An example of suitable aluminium is that having a purity of 98.7%.

In step (C) the reaction of dissolution of the metallic aluminium is exothermic, wherefore aluminium is to be added gradually in a time generally comprised between 30 and 240 minutes and by controlling the temperature so that it does not exceed 105°C.

At the end of the reaction the solution is kept under stirring at 80-105°C to complete the aluminium dissolution.

The solutions obtained by the process according to the present invention result limpid, without opalescence and show a stability of at least three months like the commercial solutions having the same basicity used for waters treatment.

Some examples are now given for illustrative purposs.

EXAMPLE 1

In a 2 l flask, 335 g of ALPOCLAR(R) 200 type (a) are introduced, which consists of an aqueous solution of basic aluminium chlorosulphate having an Al_2O_3 title of 17.2% by weight, a content in Cl ions of 21.6% by weight, a content in SO_4 ions of 1.3% by weight and a 37% basicity.

150 g of water are subsequently introduced in order to have a solution with an Al_2O_3 title of 12.09% by weight.

The obtained solution is acidified by addition of 20.8 g of 96% H_2SO_4, and keeping it under stirring, it is heated to 85-95°C.

When such a temperature is reached, 22 g of metallic aluminium chips are slowly added to the solution kept under stirring, by maintaining the reaction temperature at 85°-95°C.

When the addition of metal aluminium is ended, in a time of 30-60 minutes, the reaction mixture is kept under stirring at a temperature of 85°-95°C for further 3 hours to complete the dissolution of the metallic aluminium.

The obtained solution is then diluted with 452 g of water to have a final solution with an Al_2O_3 title of 10.26% by weight.

The final solution of basic aluminium chlorosulphate has an Al_2O_3 title of 10.26% by weight, a content in Cl ions of 7.67% by weight, a content in SO_4 ions of 2.42% by weight, a Cl/Al molar ratio of 1.07, a SO_4/Al molar ratio of 0.13 and a basicity of 56%.

The obtained solution appears limpid and results stable for at least 3 months.

EXAMPLES 2-7

The procedure of Example 1 was repeated by using the amounts of ALPOCLAR(R) 200 type (a), of metallic Al, of H_2SO_4 and of initial and final dilution H_2O as reported in Table 1.

The characteristics of the obtained solutions of basic aluminium chlorosulphate are reported in Table 1.

Said solutions appear limpid and result stable for at least 3 months.

EXAMPLE 8 (comparative)

The procedure of Example 1 was repeated by using the amounts of ALPOCLAR(R) 200 type (a), of metallic Al, of H_2SO_4 and of initial and final dilution H_2O as reported in Table 1.

It results therefrom that the solution put to react has an Al_2O_3 title of 11.46% by weight and that the molar ratio between the added metallic Al and Al_2O_3 of the solution is 1.98.

The characteristics of the obtained solution of basic aluminium chlorosulphate are reported in Table 1.

Said solution appears opalescent and does not result stable.

EXAMPLE 9

Example 1 was repeated with the difference that the final dilution with water was not carried out.

The characteristics of the obtained solution of basic aluminium chlorosulphate having high Al_2O_3 title (18.73%) are reported in Table 1.

Said solution appears limpid and results stable for at least 3 months.

EXAMPLE 10 (comparative)

Example 9 was repeated with the difference that 100 g of initial dilution water were employed instead of 150 g.

It results therefrom that the solution put to react with metallic Al has an Al_2O_3 title of 13.42% by weight.

The characteristics of the obtained solution of basic aluminium chlorosulphate are reported in Table 1. Said solution appears opalescent and does not result stable.

EXAMPLES 11-13

The procedure of Example 1 was repeated by using the amounts of ALPOCLAR(R) 200 respectively of type (b), (c) and (d), of metallic Al, of H_2SO_4 and of water of initial and final dilution water as reported in Table 1.

The obtained solutions of basic aluminium chlorosulphate having the characteristics reported in Table 1, appear limpid and result stable for at least 3 months.

EXAMPLE 14

Example 1 was repeated with the difference that H_2SO_4 was added to the solution after the dissolution reaction of the metallic Al has been carried out, instead before such reaction.

The obtained solution of basic aluminium chlorosulphate shows the same characteristics and the same stability of the solution obtained according to example 1.

EXAMPLE 15

Example 1 was repeated with the difference that the dissolution reaction of the metallic Al was carried out at a temperature of 105°C instead of at 85°-95°C.

A solution of basic aluminium chlorosulphate was obtained having the same characteristics and stability of the solution obtained in example 1.

EXAMPLE 16

Example 15 was repeated with the difference that the H_2SO_4 was added to the solution after the dissolution reaction of the metallic Al has been carried out.

A solution of basic aluminium chlorosulphate was obtained having the same characteristics and stability of the solution obtained in example 1.

Table 1

Ex.	Reaction conditions					Final solution						
	Temp. °C	ALPOCLAR 200 type *	Al g	N_2SO_4 96% g	H_2O initial g	H_2O final g	Al_2O_3 % by wt	Cl % by wt	SO_4 % by wt	Basicity %	Molar Cl/Al	Molar SO_4/Al	Appearance	Stability months
1	85-95	(a) 355	22	20.8	150	452.2	10.26	7.67	2.42	56	1.07	0.13	limpid	3
2	85-95	(a) 335	23.8	20.8	150	470.4	10.26	7.24	2.39	58	1.01	0.12	limpid	3
3	85-95	(a) 400	17.9	20.8	150	411.3	10.26	8.64	2.48	51	1.21	0.13	limpid	3
4	85-95	(a) 355	22	23.0	150	450	10.26	7.67	2.62	55	1.07	0.14	limpid	3
5	85-95	(a) 355	22	25.0	150	448	10.26	7.67	2.81	55	1.07	0.15	limpid	3
6	85-95	(a) 355	22	15.0	150	458	10.26	7.67	1.87	58	1.07	0.10	limpid	3
7	85-95	(a) 355	22	0.0	150	473	10.26	7.67	0.46	63	1.07	0.02	limpid	3
8 comp.	85-95	(a) 300	27	20.8	150	502.2	10.26	6.48	2.35	62	0.91	0.12	opale-scent	unstable
9	85-95	(a) 355	22	20.8	150	0.0	18.73	14.00	4.42	56	1.07	0.13	limpid	3
10 comp.	85-95	(a) 355	22	20.8	100	0.0	20.61	15.40	4.86	56	1.07	0.13	opale-scent	unstable
11	85-95	(b) 384	19.3	20.8	150	425.9	10.25	7.68	2.46	56	1.08	0.13	limpid	3
12	85-95	(c) 333	24	20.8	150	472.2	10.26	7.66	2.39	56	1.07	0.12	limpid	3
13	85-95	(d) 365	21	26.0	150	438	10.24	7.67	2.45	56	1.07	0.13	limpid	3

*

ALPOCLAR 200 type	Al_2O_3 % by wt.	Cl % by wt.	SO_4 % by wt.	Basicity %	Molar Cl/Al	Molar SO_4/Al
(a)	17.2	21.6	1.3	37	1.80	0.04
(b)	17.2	20.0	1.3	42	1.67	0.04
(c)	17.2	23.0	1.3	33	1.92	0.04
(d)	17.2	21.0	0.0	42	1.75	0,00

Claims

1. Process for preparing stable aqueous solutions of basic aluminium chlorosulphate or of basic aluminium chloride having a Cl/Al molar ratio from 0.90 to 1.22, a SO_4/Al molar ratio from 0.02 to 0.15 related to the basic aluminium

chlorosulphate, a 50-65% basicity, according to the formula

$$\frac{\%\text{ by weight } Al_2O_3/17-(\%\text{ by weight Cl}/35.5 + \%\text{ by weight } SO_4/48)}{\%\text{ by weight } Al_2O_3/17} x100,$$

an Al_2O_3 title up to 19% by weight and a content of Ca lower than 0.05% by weight, comprising:

A) dilution with water of aqueous solutions of basic aluminum chlorosulphate or basic aluminum chloride having a Cl/Al molar ratio comprised between 1.6 and 2.0, a SO_4/Al molar ratio from 0.0 to 0.05, a basicity from 33 to 42% and an Al_2O_3 title of about 17% by weight, until diluted solutions having an Al_2O_3 title from 11.8 to 13% by weight, are obtained;
B) acidification of the solution obtained in (A) with H_2SO_4 in amounts from 0 to 0.41 moles per mole of Al_2O_3 of the solution;
C) heating the solution at a temperature from 80° to 105°C and subsequent slow addition of from 0.9 to 1.98 gramatoms of subdivided metallic aluminium per mole of Al_2O_3 of the solution, by maintaining the reaction tenmperature at values not higher than 105°C, until complete dissolution of the metallic aluminium;
D) optional dilution with water of the solution obtained in (C) until an Al_2O_3 title of about 10% by weight is obtained.

2. Process acording to claim 1, wherein the acidification step (B) with H_2SO_4 is carried out after the reaction step (C).

3. Process according to claims 1 or 2, wherein the reaction step (C) by using metallic Al is carried out at temperatures from 80° to 95°C.